# System Level Analysis of Hydrogen Storage Options


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# Overview

## Timeline

- Project start date: Oct 2009
- Project end date: Sep 2014
- Percent complete: 50%

## Barriers

- $H_2$ Storage Barriers Addressed:
  - A: System Weight and Volume
  - B: System Cost
  - C: Efficiency
  - E: Charging/Discharging Rates
  - J: Thermal Management
  - K: Life-Cycle Assessments

## Budget

- FY11: $640 K
- FY12: $700 K

## Partners/Interactions

- Storage Systems Analysis Working Group (SSAWG)
- Hydrogen Storage Engineering Center of Excellence (HSECoE)
- LLNL, PNNL, SA
- Ford, University of Oregon
- TIAX, LANL, BNL, SRNL

# Objectives and Relevance

- Conduct independent systems analysis for DOE to gauge the performance of $H_2$ storage systems
- Provide results to material developers for assessment against performance targets and goals and help them focus on areas requiring improvements
- Provide inputs for independent analysis of costs of on-board systems.
- Identify interface issues and opportunities, and data needs for technology development
- Perform reverse engineering to define material properties needed to meet the system level targets

# Approach

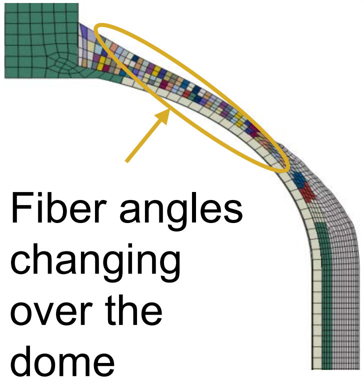
- Develop thermodynamic and kinetic models of processes in physical, complex metal hydride, sorbent, and chemical $H_2$ storage systems
  - Address all aspects of on-board and off-board storage targets, including capacity, charge/discharge rates, emissions, and efficiencies
  - Assess improvements needed in materials properties and system configurations to achieve storage targets
- Select model fidelity to resolve system-level issues
  - On-board system, off-board spent fuel regeneration, reverse engineering
  - Conduct trade-off analyses, and provide fundamental understanding of system/material behavior
  - Calibrate, validate, and evaluate models
- Work closely with DOE technology developers, HSECoE and others in obtaining data
- Participate in SSAWG meetings and communicate modeling, analysis approach, and results to foster consistency among DOE-sponsored analysis activities

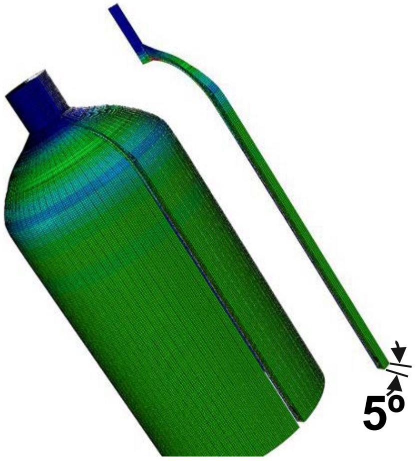
# Summary: FY2012 Technical Accomplishments

1. Compressed $H_2$ storage
   - Carbon fiber requirements: ABAQUS simulations
   - Fast fill: CFX simulations
   - Cost study: Input to SA
2. Cryo-compressed $H_2$ storage
   - Dormancy enhancement by natural para-to-ortho conversion
3. $H_2$ storage in MOF-5 (wrapped up)
   - Capacity enhancement by catalyzed para-to-ortho conversion
4. $H_2$ storage in alane (on-board system analysis wrapped up)
   - Off-board regeneration by organo-metallic (BNL) and electrochemical routes (SRNL)
5. $H_2$ storage in ammonia borane (on-board system analysis wrapped up)
   - AB regeneration: benzophenone route for hydrazine production
6. $H_2$ storage in CBN (in cooperation with University of Oregon)
   - Reaction kinetics and conversion in catalytic reactors

# Compressed $H_2$ Storage

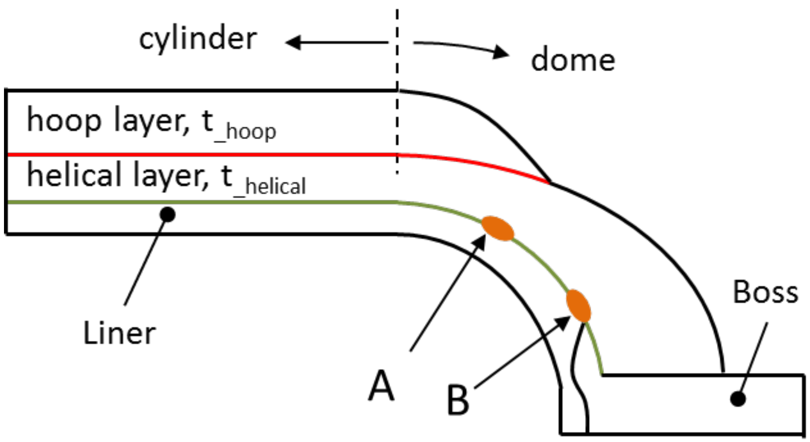
- Carbon fiber in $cH_2$ tanks accounts for >75% of onboard system cost and ~60% of system weight. Reducing the amount of CF usage is one of DOE's major initiatives in physical storage
- ANL is performing analyses to identify opportunities for CF savings
- ABAQUS 6.11-2 with Wound Composite Modeler extension
- Set up 5º azimuthal strip FE model
  - Geodesic dome shape with varying fiber angles over dome
  - Non-linear analysis
  - 3D quadratic solid elements
  - Cyclic boundary conditions on 5º azimuthal strip
  - Symmetric boundary conditions along axial direction

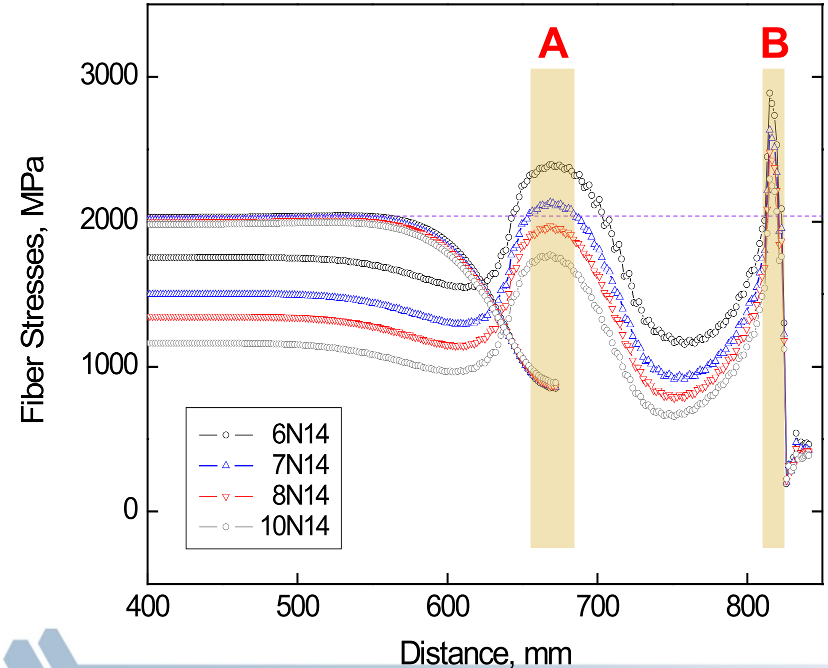


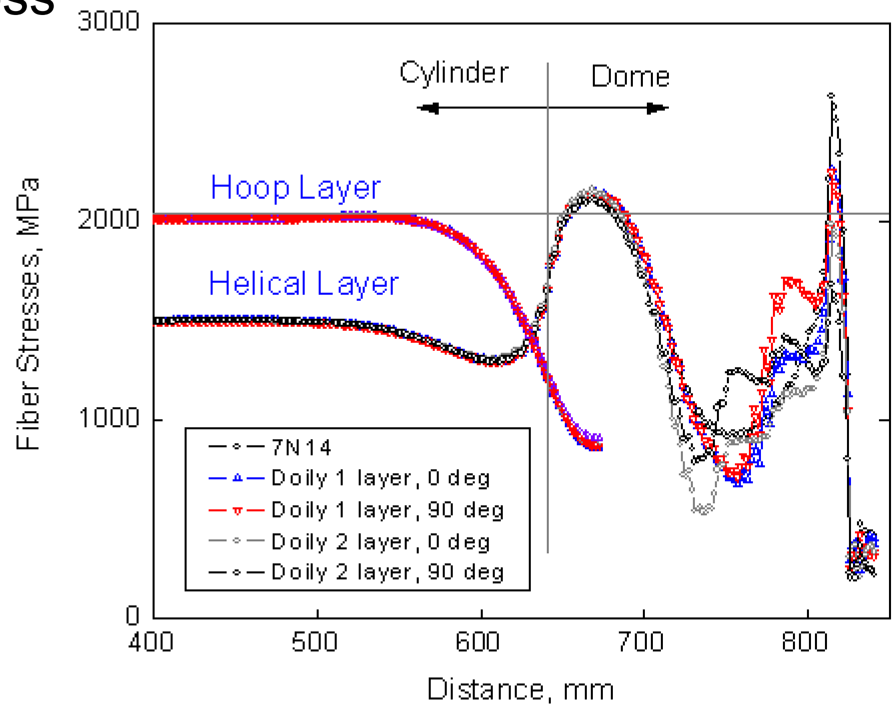



# Determination of Hoop and Helical Layer Thicknesses

- High stress locations
  - Cylinder, shoulder, boss
- Need sufficient hoop and helical layers to protect all three high stress locations
  - Hoop layers to protect cylinder, helical layers to protect dome
  - Add "doilies" to reinforce boss

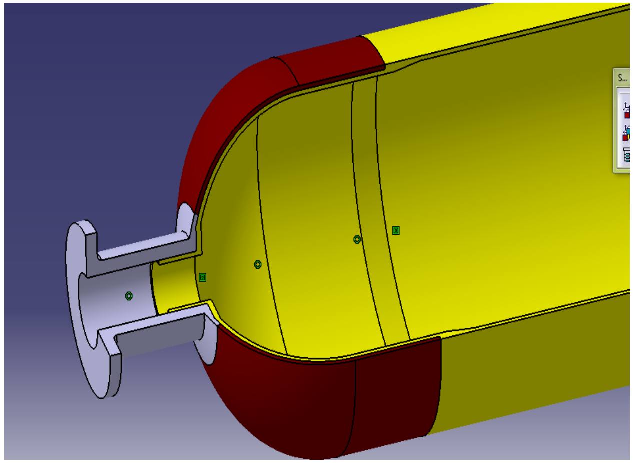


# Optimization of CF Usage

- Filament winding only
  - Number of helical layers wound through cylindrical section is more than necessary to absorb the axial stress
- Integrated End Cap Vessel (IECV)
  - Reduce number of helical layers in filament winding
  - Reinforce domes with end caps made of carbon fibers by resin transfer molding (RTM)
  - Blow molding of end cap and boss with liner
  - Optimize end cap shape and weight to minimize stress concentration at liner interface

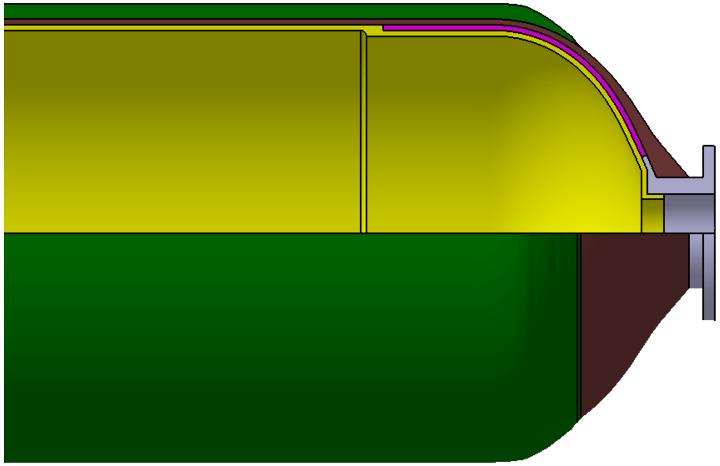


- Conducting trade-off analyses to relate CF cost, manufacturing processes, and weight and volume

# Filament Winding Over End Caps

Filament winding over end caps

- Carbon-fiber end caps
  Thickness = 5 mm, weight = 4.6 kg
- Determined minimum number of helical windings for design load
- 18% reduction in CF composite weight vs. base case (filament winding only)

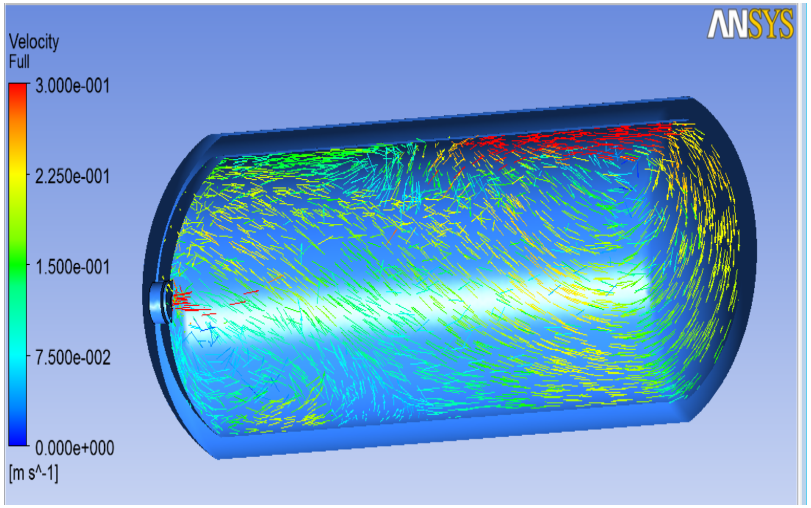


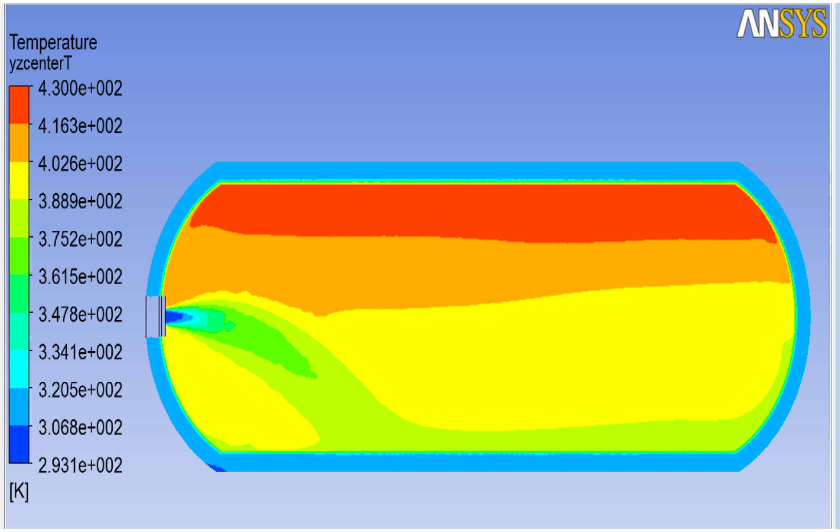
| Case | FE Model | Helical Thickness | Hoop Thickness | CF Composite | CF Composite Reduction | Remarks |
|---|---|---|---|---|---|---|
| ID | ID | mm | mm | kg** | wt% | |
| Base | SB-10N14 | 10.4 | 14.8 | 75.9 | - | No end caps |
| 1 | SB-8N14-EC | 8.8 | 14.8 | 74.4 | 2 | 5-mm end caps |
| 2 | SB-7N14-EC | 7.8 | 14.8 | 70.8 | 6.7 | 5-mm end caps |
| 3 | SB-6N14-EC | 6.5 | 14.8 | 66.1 | 12.9 | 5-mm end caps |
| 4 | SB-5N14-EC | 5.5 | 14.8 | 62.6 | 17.5 | 5-mm end caps |

**Main assumptions: 2550 MPa tensile strength; 80% translation efficiency; 60% fiber volume; 1 helical/hoop stress ratio; 2.25 safety factor

# Analysis of 70-MPa Fast Fill with CFX

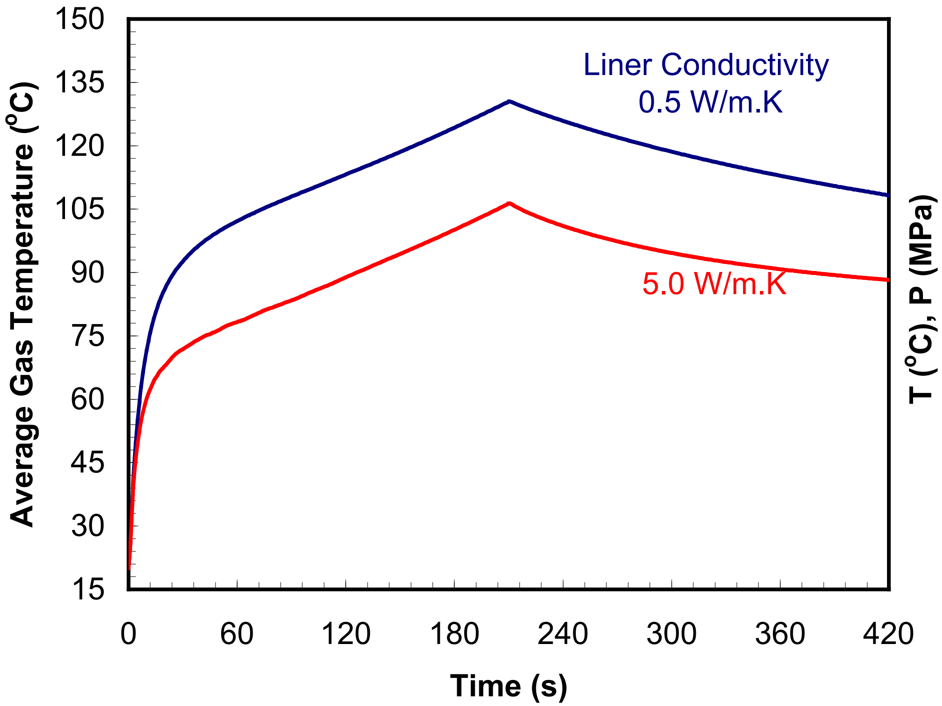
- Pre-cooling at fueling station is needed for 70-MPa fast fill
- Investigate ways to reduce or eliminate pre-cooling
  - Increase HDPE and CF composite thermal conductivities
  - Promote mixing with new fill tube designs
- CFX simulations
  - 1.5 kg/min refueling rate
  - Initial P = 2 MPa, T = 20°C
  - 5-mm HDPE liner, 0.5 W/m.K
  - 2.6-cm T700S, 9.4 W/m.K
  - Inlet $H_2$ T = -40°C to 20°C
  - 5 $W/m^2$.K external heat transfer coefficient

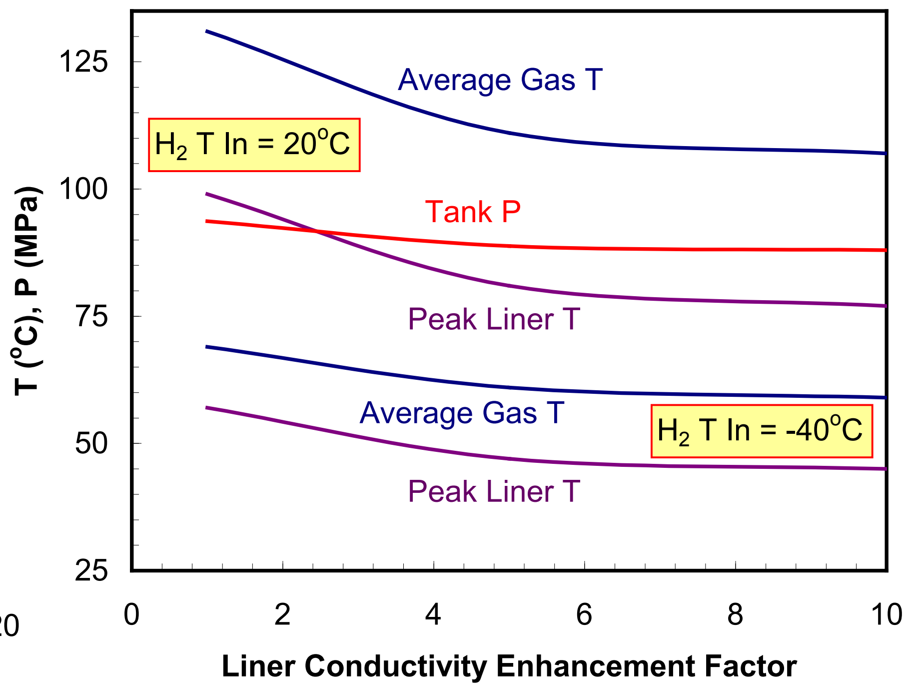


# Effect of Liner Thermal Conductivity on Temperature

- A five-fold to ten-fold increase in the HDPE liner thermal conductivity has the potential to reduce the liner temperature by up to 20°C
  - Liner temperature < 85°C with ambient fuel temperature
  - Six-fold increase in conductivity with 30% SWNT in HDPE*
- Increase in CF composite conductivity has insignificant impact

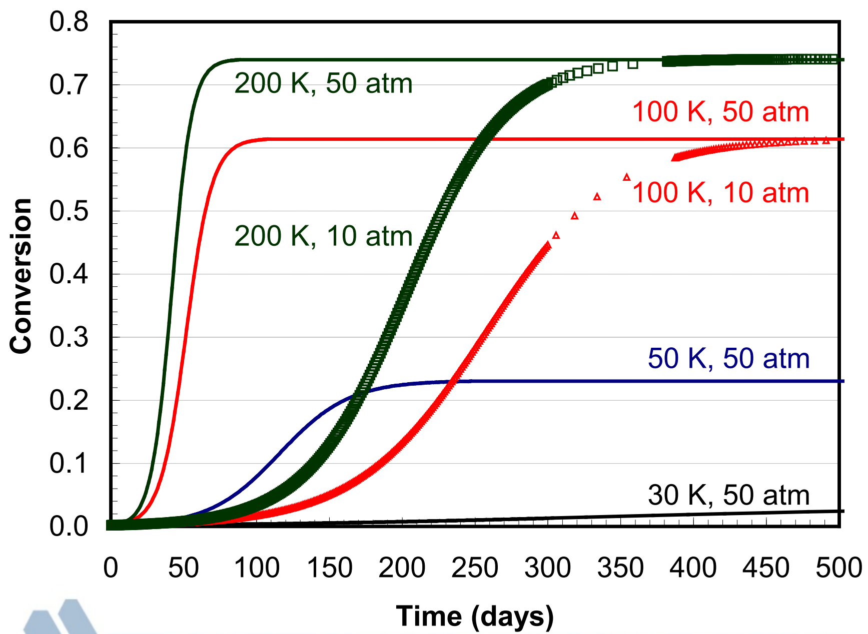


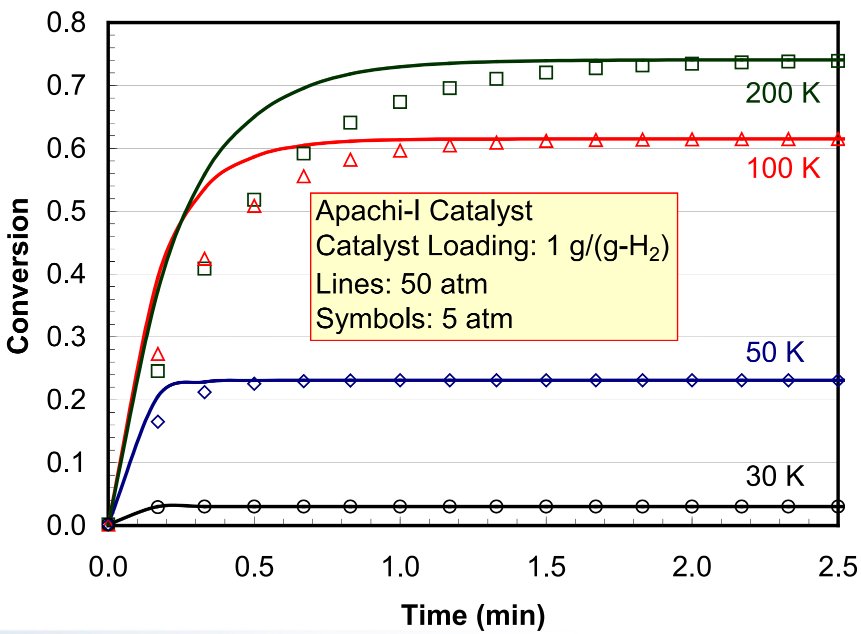




* Haggenmuler et al., "Single Wall Carbon Nanotube/Polyethelene Nanocomposites: Thermal and Electrical Conductivity," Macromolecules, 2007, 40, 2417-2421

# Thermodynamics & Kinetics of Para-Ortho Conversion

- A tank charged with para $LH_2$ can potentially absorb 524 $kJ.kg^{-1}$ as $pH_2$ is converted to $nH_2$ (25% para)
- Extremely slow gas phase conversion of $pH_2$ to $oH_2$
  - May help extend dormancy since rate increases with P and T
- Rapid catalytic conversion on commercial Ni-on-silica catalyst
  - Time constant of the order of refueling time
- FitzGerald, Physical Rev. B 81, 104305 (2010): $oH_2$ converts to $pH_2$ on occupied sites in MOF-74 at 40 K within minutes but conversion is slower on MOF-5

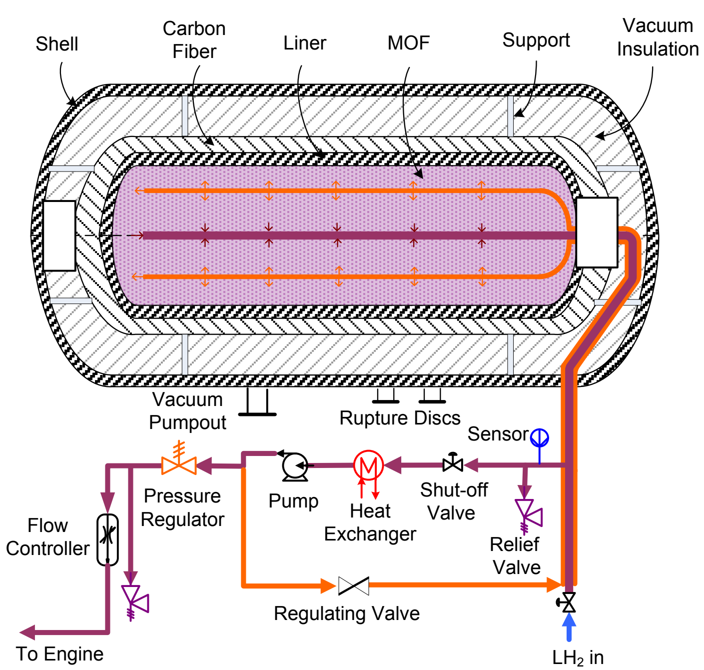


# Cryogenic Hydrogen Storage in MOF-5

Adiabatic $LH_2$ refueling

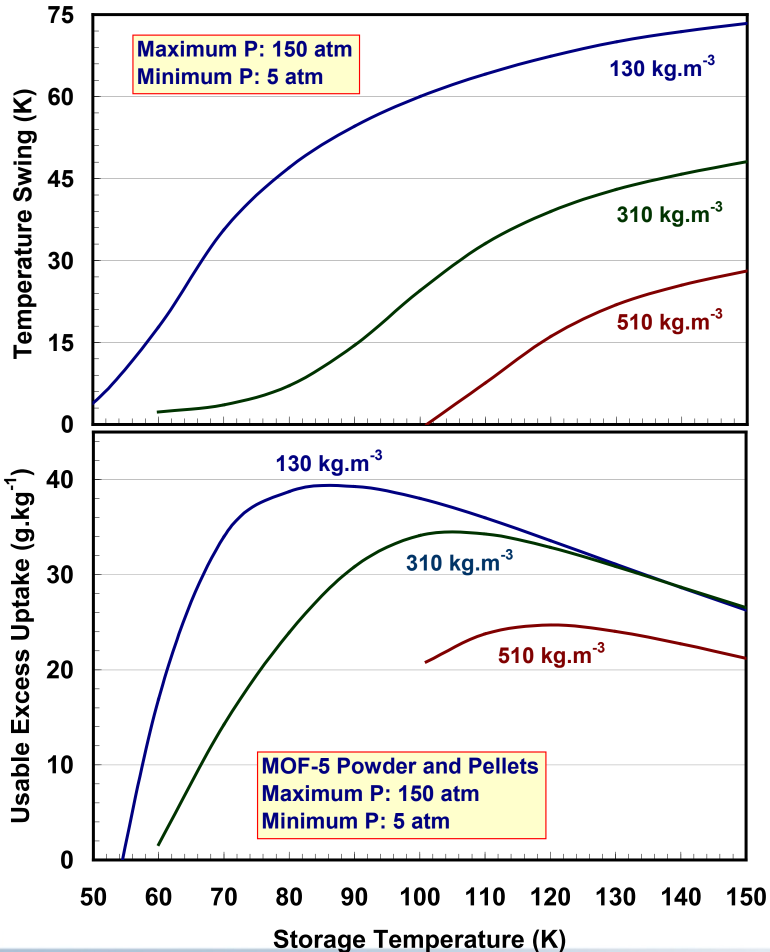
- Enhanced capacities due to endothermic cooling by $pH_2$ to $oH_2$ conversion during refueling
- Minimum bed permeability and conductivity for heating by $H_2$ recycle during discharge

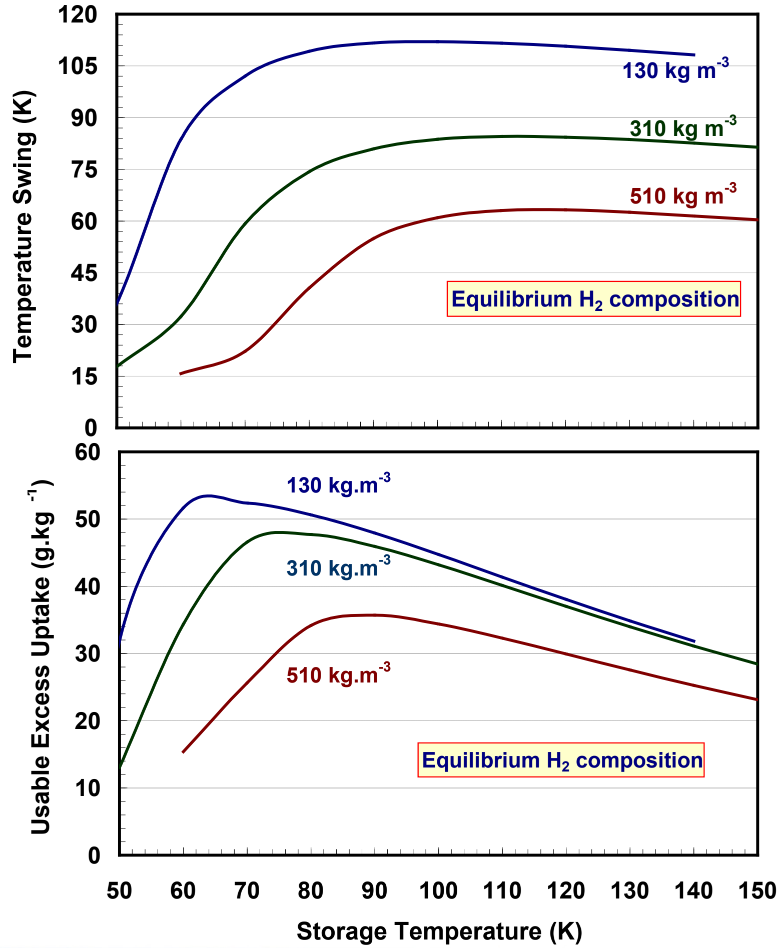



| | Parameter | Reference Values |
|---|---|---|
| **Sorbent** | **MOF-5 (Basolite Z100-H)** | Powder: Zhou, J. Phys. Chem. C 2007, 111 |
| | | Pellets: Sudik, AIChE Meeting, 2010 |
| | Skeletal density | 2030 $kg.m^{-3}$ |
| | Crystallographic density | 610 $kg.m^{-3}$ |
| | Bulk density | 130 $kg.m^{-3}$ (powder), 310-790 $kg.m^{-3}$ (pellets) |
| | Thermal conductivity | 0.088 $W.m^{-1}.K^{-1}$ |
| **Insulation** | **Multi-Layer Vac. Super Insulation** | Aluminized Mylar sheets, Dacron spacer |
| | Layer density | 28 $cm^{-1}$ |
| | Density | 59.3 $kg.m^{-3}$ |
| | Pressure | $10^{-5}$ torr |
| | Effective conductivity | $5.2x10^{-4}$ $W.m^{-1}.K^{-1}$ |
| **Tank** | **T700S Carbon Fiber** | Toray Carbon Fiber |
| | Tensile strength | 2550 MPa |
| | Density | 1600 $kg.m^{-3}$ |
| | L/D | 3 |
| | Liner | Al 6061-T6 alloy, 5500 PT cycles, 125% NWP |
| | Shell | 3.2-mm thick Al 6061-T6 alloy alloy |
| **Refueling** | **Adiabatic Refueling with $LH_2$** | |
| | $LH_2$ pump efficiency | 60-70% |
| | Storage temperature | Function of storage pressure |
| | Temperature swing | Function of storage pressure and temperature |
| **Discharge** | **$H_2$ Recirculation** | |
| | Temperature | 273 K |
| | Recirculation rate | TBD |
| **Balance of System** | Miscellaneous weight | 16 kg |
| | Miscellaneous volume | 10 L |

# Adiabatic Refueling of MOF-5 Powder and Pellets

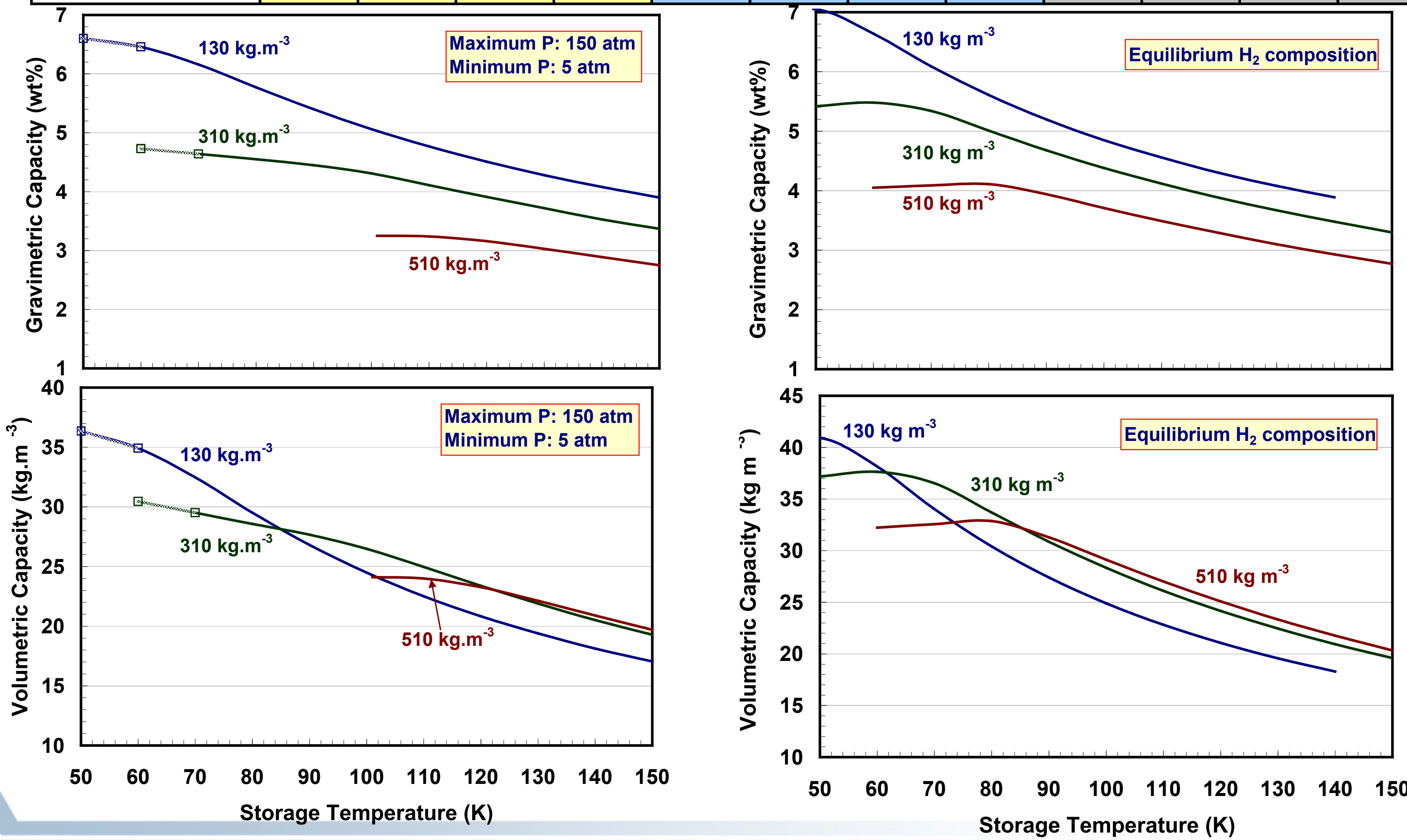
| Storage P | Storage T | ΔT | $N_{exr}$ | Storage T | ΔT | $N_{exr}$ | Storage T | ΔT | $N_{exr}$ |
|---|---|---|---|---|---|---|---|---|---|
| 150 atm | K | K | $g.kg^{-1}$ | K | K | $g.kg^{-1}$ | K | K | $g.kg^{-1}$ |
| Bulk Density | $130\ kg.m^{-3}$ | | | $310\ kg.m^{-3}$ | | | $510\ kg.m^{-3}$ | | |
| Frozen $H_2$ | 80 | 47 | 38.7 | 110 | 33 | 34.3 | 120 | 16 | 24.7 |
| Equilibrium $H_2$ | 70 | 102 | 52.4 | 80 | 74 | 47.7 | 90 | 55 | 35.7 |



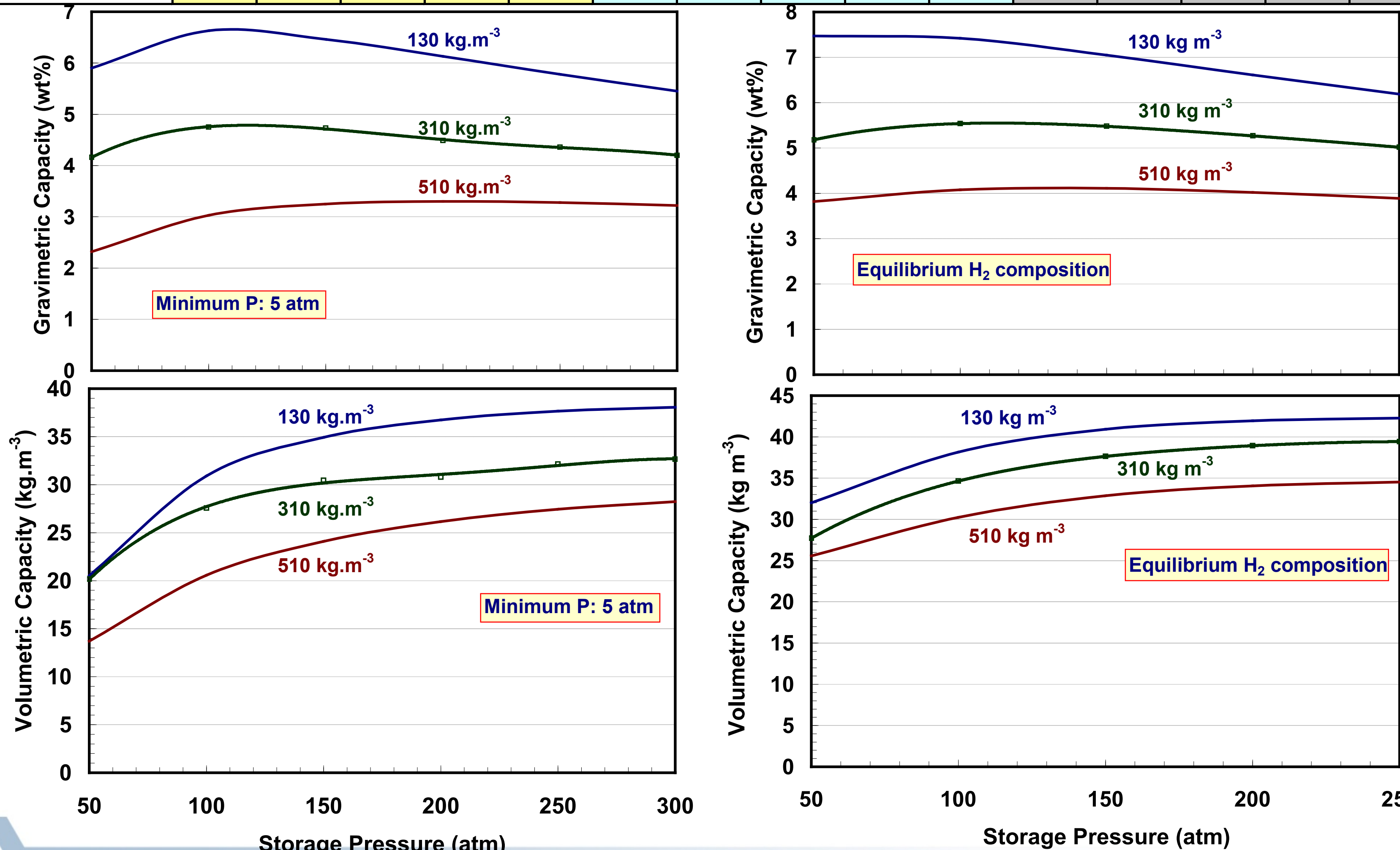
# System Storage Capacity: MOF-5 Powder & Pellets

| Storage P | T | ΔT | System | | T | ΔT | System | | T | ΔT | System | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 150 atm | K | K | wt% | $kg.m^{-3}$ | K | K | wt% | $kg.m^{-3}$ | K | K | wt% | $kg.m^{-3}$ |
| Bulk Density | $130\ kg.m^{-3}$ | | | | $310\ kg.m^{-3}$ | | | | $510\ kg.m^{-3}$ | | | |
| Frozen $H_2$ | 60 | 18 | 6.5 | 34.9 | 70 | 4 | 4.6 | 29.5 | 101 | 0 | 3.3 | 24.1 |
| Equilibrium $H_2$ | 50 | 36 | 7.1 | 40.9 | 60 | 32 | 5.5 | 37.6 | 80 | 41 | 4.1 | 32.9 |



# MOF-5 System Capacity: Effect of Storage Pressures

| | P | T | ΔT | System | | P | T | ΔT | System | | P | T | ΔT | System | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | atm | K | K | wt% | $kg.m^{-3}$ | atm | K | K | wt% | $kg.m^{-3}$ | atm | K | K | wt% | $kg.m^{-3}$ |
| Bulk Density | $130\ kg.m^{-3}$ | | | | | $310\ kg.m^{-3}$ | | | | | $510\ kg.m^{-3}$ | | | | |
| Frozen $H_2$ | 100 | 60 | 29 | 6.6 | 30.9 | 110 | 60 | 5 | 4.8 | 27.6 | 200 | 102 | 0 | 3.3 | 26.2 |
| Equilibrium $H_2$ | 100 | 50 | 49 | 7.4 | 38.2 | 100 | 50 | 18 | 5.5 | 34.6 | 150 | 80 | 41 | 4.1 | 32.9 |



# $H_2$ Storage in CBN Heterocycle Materials

Data from S-Y Liu, U. Oregon, ST038

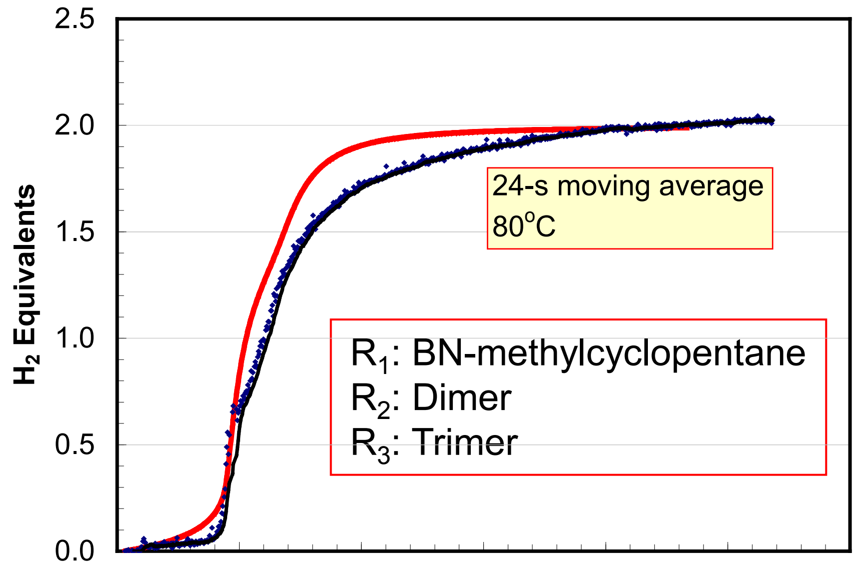
$$2R_1 = R_2 + 2\alpha_1 H_2$$

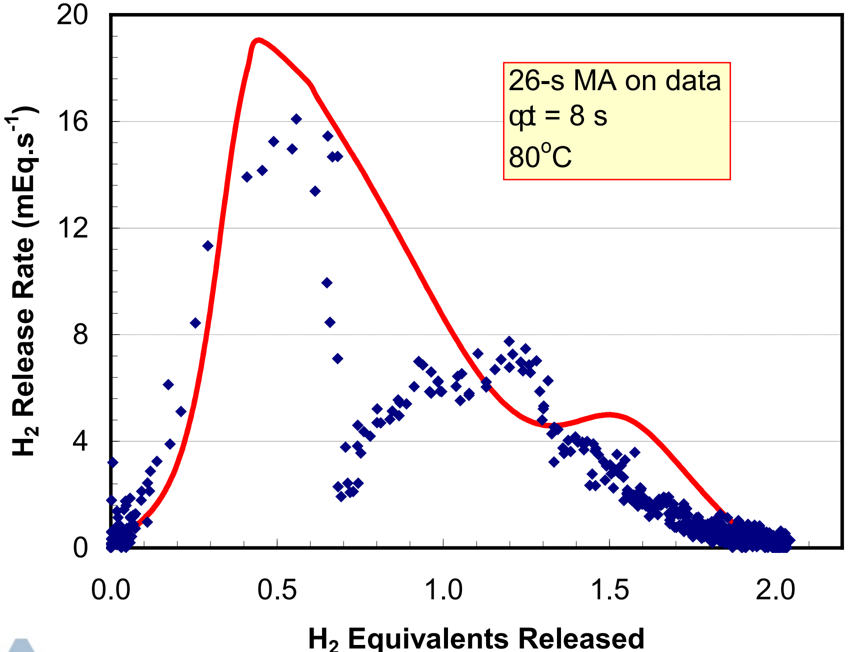
$$3R_2 = 2R_3 + 2\alpha_2 H_2$$

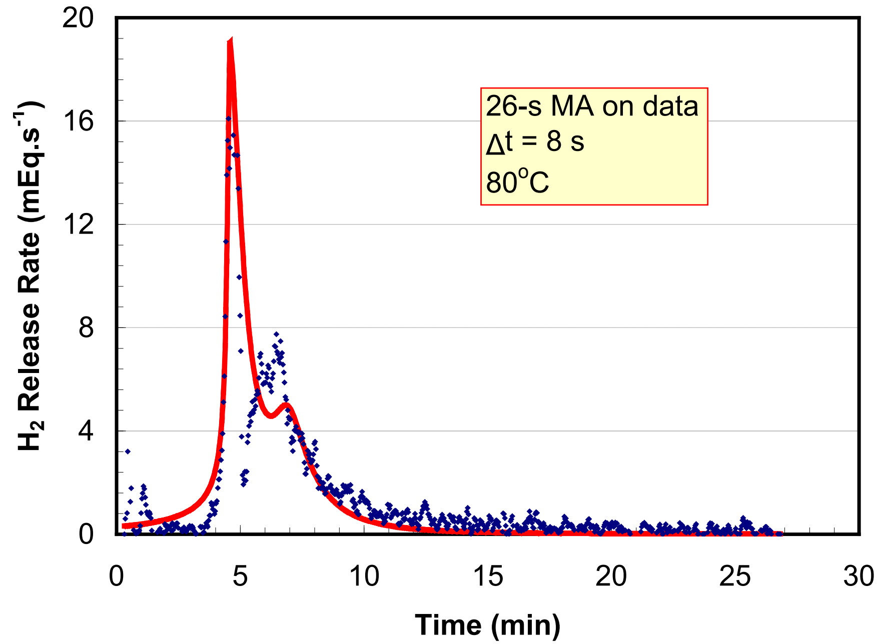
$$\alpha_1 = 1,\ \alpha_2 = 3$$

Peaks in derived reaction rates

- Self-inhibited catalytic reactions
- Consistent conversions at lower 3 and 1 mol% catalyst loadings



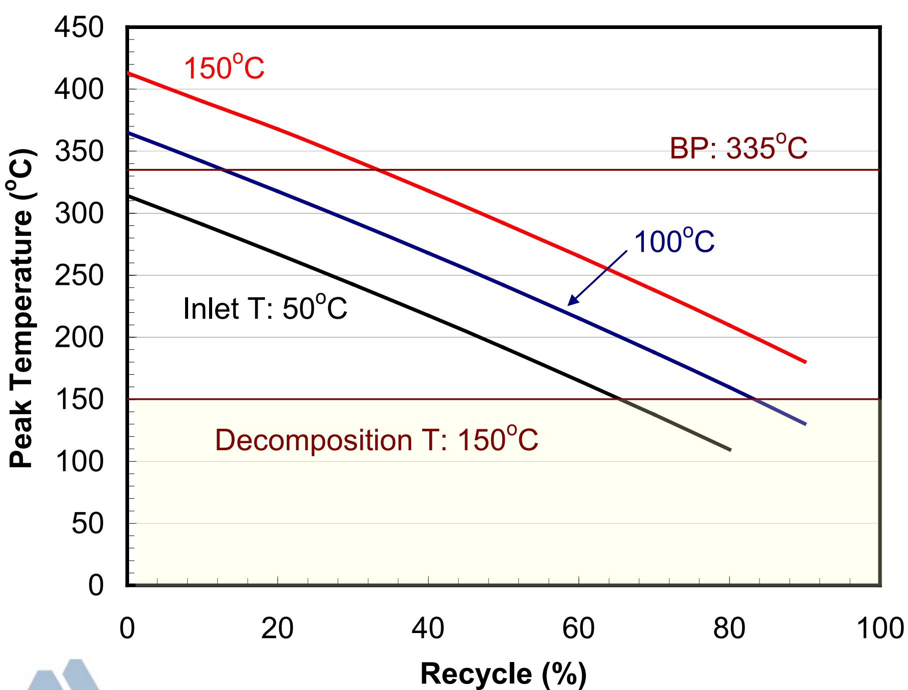



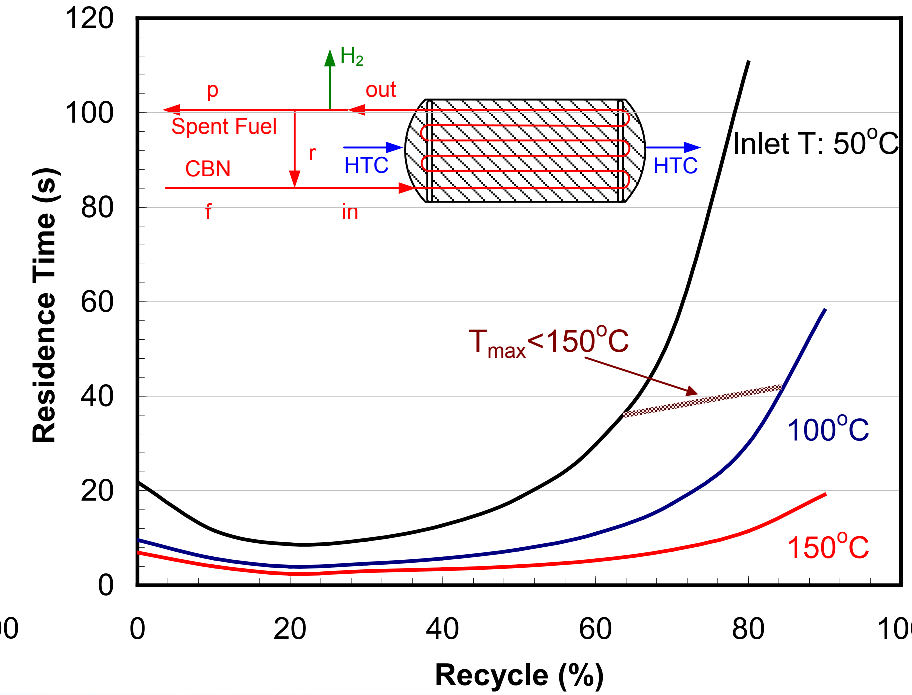




W. Luo, P.G. Campbell, L.N. Zakharov, S-Y Liu, J. Am. Chem. Soc., 133 (2011) 19326 - 19329

# CBN Reactor Performance

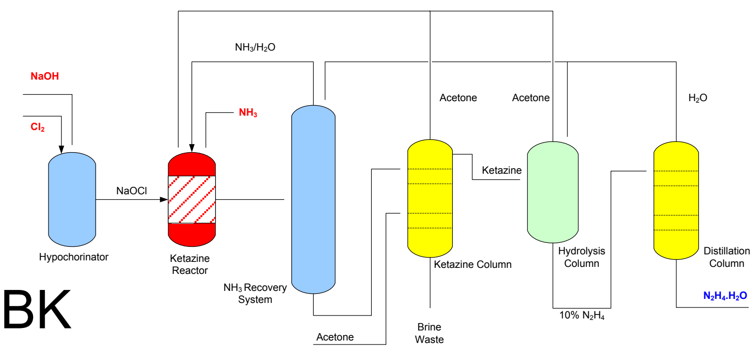
- Need 65 - 85% spent CBN recycle to maintain peak reactor temperature below 150°C (decomposition temperature)
  - $\Delta h$ = 18-20 kJ.mol-$H_2^{-1}$
- Need more rapid or dispersed catalyst for conversion in < 10 s at 150°C (more active catalysts identified by Luo)
- Next steps
  - Mechanism-based rates, complete system analysis
  - Alternate catalysts, rate data at 120°C and with dilute feeds



# AB Regeneration Using Hydrazine

- LANL has developed a one-pot process for regenerating spent AB using hydrazine ($N_2H_4$) as the limiting reagent in liquid ammonia
  - $BNH_2 + N_2H_4 \rightarrow BH_3NH_3 + N_2$
- Analyzed three methods of hydrazine production
  - Bayer Ketazine, feed materials: $Cl_2$, NaOH, and $NH_3$ (commercial)
  - PCUK process, feed materials: $H_2O_2$ and $NH_3$ (commercial)
  - Benzophenone process, feed materials: $NH_3$ (verified in the lab)

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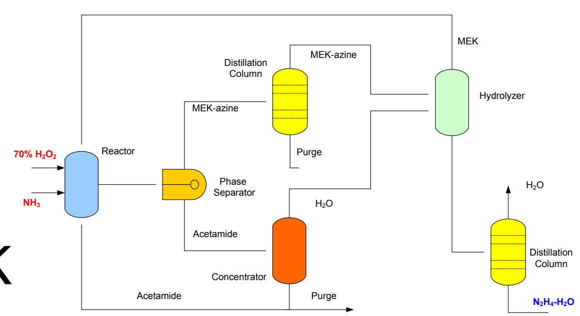
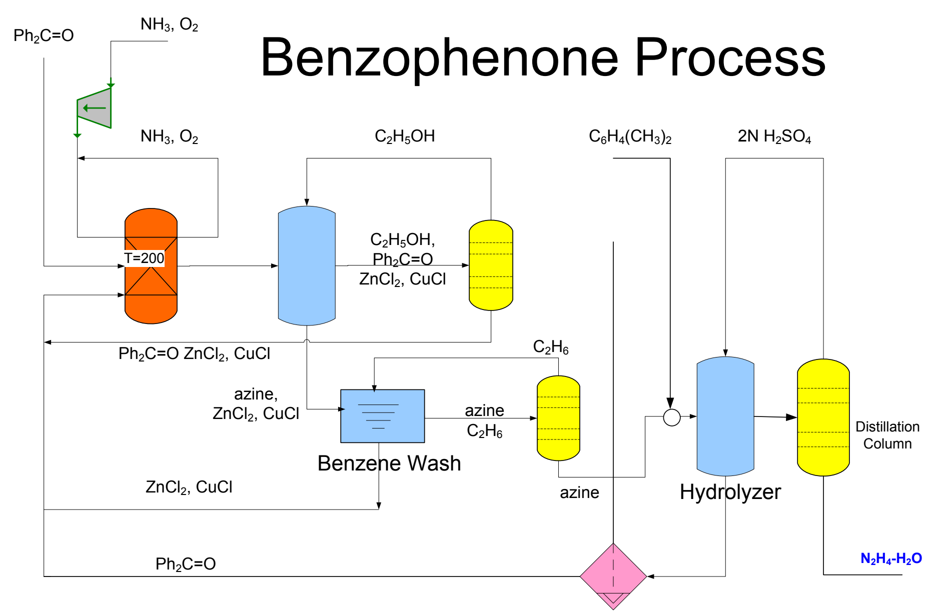



PCUK

Benzophenone Process



# FCHtool Analysis: AB Regeneration Using Hydrazine

- One-third of $H_2$ needed to make $N_2H_4$ from $NH_3$ forms $H_2O$
- BK: Excessive amount of electricity required to produce $NaOH/Cl_2$
- PCUK: Large amount of steam consumed in making $H_2O_2$
- Benzophenone Process: 50% higher efficiency, 33% less emissions than in PCUK

| Process | PCUK | | Bayer | | Benzophenone | |
|---|---|---|---|---|---|---|
| | NG | Electricity | NG | Electricity | NG | Electricity |
| $NH_3$ Production | 258 | 5 | 169 | 5 | 258 | 5 |
| $H_2O_2$ Production | 331 | - | - | - | - | - |
| $NaOH/Cl_2$ Production | - | - | 65 | 870 | - | - |
| Hydrazine Production | 227 | - | 246 | - | 253 | - |
| AB Regeneration | 45 | 104 | 45 | 104 | 45 | 104 |
| Total Primary Energy (MJ) | 861 | 109 | 525 | 979 | 556 | 109 |
| WTT Efficiency (%) | 12.4 | | 8.0 | | 18.1 | |

- GHG emissions, g/kg-$H_2$ in AB

| AB Regeneration | VOC | CO | $NO_x$ | $PM_{10}$ | $SO_x$ | $CH_4$ | $N_2O$ | $CO_2$ | GHGs |
|---|---|---|---|---|---|---|---|---|---|
| **Hydrazine - Ketazine** | 9.5 | 28.6 | 97.4 | 85.6 | 156.0 | 177.3 | 1.4 | 96866 | 101350 |
| **Hydrazine - PCUK** | 6.5 | 18.9 | 52.2 | 14.1 | 25.6 | 148.0 | 0.7 | 59290 | 62913 |
| **Hydrazine - Benzophenone** | 4.3 | 12.3 | 33.8 | 12.4 | 22.0 | 93.6 | 0.5 | 39762 | 42051 |

# Collaborations

| | |
|---|---|
| Compressed $H_2$ (cH2) | PNNL, SA |
| Cryo-Compressed $H_2$ (CcH2) | LLNL, BMW |
| Metal Hydrides | BNL |
| Chemical Hydrides | LANL, University of Orgeon |
| Sorbents | Ford |
| GHG Emissions | ANL (GREET) |
| Off-Board Spent Fuel Regeneration | BNL, LANL, SRNL |
| Off-Board Cost | ANL (H2A Group), ANL (HDSAM) |
| On-Board Cost | TIAX, SA |
| SSAWG | HSECoE, DOE, LLNL, OEMs,Tank Manufactures, SA, TIAX |

– Argonne develops the storage system configuration, determines performance, identifies and sizes components, and provides this information to TIAX and SA for manufacturing cost estimation

# Future Work

Physical Storage

- Propose and analyze methods of reducing carbon fiber (CF) content (doilies, end caps, winding angle) and cost of 700-bar storage tanks (SA collaboration)
- Validate results on CF reduction methods with laboratory data on coupons (mechanical properties)
- Validate finite element model against experimental and field data (collaboration with PNNL led project)
- Improved nozzles and liners for fast-fill (analysis and validation)
- Supercritical cryo-compressed storage concepts (LLNL)

Material Based Storage

- Provide system analysis support (catalytic activity, reactor, operating conditions) to U Oregon effort to develop CBN heterocycle materials
- Develop flowsheets and determine efficiencies of proposed spent CBN regeneration chemistries

Off-board Analyses

- Fuel cycle efficiency of alane/AB regeneration (SRNL collaboration)

# Project Summary

| | |
|---|---|
| Relevance: | Independent analysis to evaluate on-board and off-board performance of materials and systems |
| Approach: | Develop and validate physical, thermodynamic and kinetic models of processes in physical and material-based systems<br>Address all aspects of on-board and off-board targets including capacities, rates and efficiencies |
| Progress: | Analyzed methods to achieve 20% reduction in CF requirement for 700-bar storage vessels<br>Proposed method to reduce or eliminate pre-cooling in fast fill<br>Enhanced capacity of $LH_2$ refueled MOF-5 system by 10-40% through catalytic $pH_2$-to-$oH_2$ conversion<br>Determined optimum conditions for $H_2$ discharge from a promising CBN material<br>Analyzed benzophenone process for 50% increase in AB regeneration efficiency |
| Collaborations: | SSAWG, HSECoE, LANL, LLNL, PNNL, U. Oregon, TIAX, SA |
| Future Work: | Propose, analyze and validate methods of reducing cost of CF wound storage tanks<br>Provide system analysis support to U. Oregon project on development of CBN heterocycle materials |